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Robert J. Remick
Engineering Research Division
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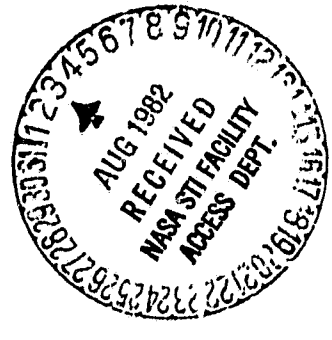
Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lewis Research Center
Under Contract DEN 3-208



for

U.S. DEPARTMENT OF ENERGY
Division of Fossil Fuel Utilization

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INTRODUCTION

This report documents work performed by the Institute of Gas Technology (IGT) for the NASA-Lewis Research Center under Contract No. DEN 3-208. This work was performed over a 15-month period from January 1981 through March 1982 and addresses the problem of platinum sintering on phosphoric acid fuel cell cathodes.

The cathode of the phosphoric acid fuel cell uses a high-surface-area platinum catalyst dispersed on a conductive carbon support to minimize both cathode polarization and fabrication costs. During operation, however, the active surface area of these electrodes decreases, which in turn leads to decreased cell performance. This loss of active surface area is a major factor in the degradation of fuel cell performance over time. For industry to accept this technology, therefore, it is important to understand this problem and develop approaches to its solution.

In the petroleum industry, supported platinum blacks are used as heterogeneous catalysts. To maximize the cost-effectiveness of these catalysts, the metal is prepared in the form of very small particles, about 10Å to 100Å in diameter. The atoms appear in significant numbers at the surface of crystallites of this size, where they are available for interaction with reactant molecules. When the particles contact one another at elevated temperatures, however, they tend to fuse together, or "sinter", causing a loss in surface area, which is detrimental to the performance of the catalyst. Considerable work has been directed toward understanding and eliminating the sintering of highly dispersed supported metal catalysts that are used in the petroleum industry. This work has led to the widespread use of porous, high-surface-area ceramic materials to support and retain the small catalyst particles.[1] This approach has also proved successful in many fuel cell applications, although the additional requirement that the support also be electronically conducting greatly limits the choice of support materials.

Several carbon blacks have been successfully used in fuel cells as supports for highly dispersed platinum black. For example, Vulcan XC-72R, which is a product of the Cabot Corporation, has proved to be an excellent support for fabricating platinum-catalyzed phosphoric acid fuel cell anodes. When the same material is used at the cathode, however, it slowly deteriorates

through oxidation. One method of rendering carbon blacks resistant to oxidation is to graphitize them at temperatures up to 3000°C. During this procedure the carbon crystal structure is reorganized into large graphite flakes. This process not only increases oxidation resistance, but also improves electronic conductivity. Unfortunately, it also reduces surface area and eliminates pore structure, thus increasing the likelihood of platinum sintering.

Until recently, however, only a few studies[2-6] addressed this problem under conditions encountered in electrochemical systems.

Three possible mechanisms by which platinum sintering could occur in electrochemical systems have been proposed[7]:

- Metal dissolution followed by redeposition at low-potential sites on the electrode
- Crystallite migration over the surface of the support material, accompanied by liquid-like coalescence of the crystallites
- Interparticle migration of single atoms.

Recent work,[8] using transmission electron micrographs of platinum deposited on carbon films, indicates that crystallite migration does in fact occur and that this is the most likely sintering mechanism for platinum supported on graphite in electrochemical systems. This program's purpose is to investigate the structural modification of the carbon support, as a means of minimizing platinum sintering at phosphoric acid fuel cell cathodes.

The IGT experimental approach is based upon first forming etch pits in the surface of the carbon support and then causing the platinum crystallites to locate in these etch pits, thus hindering their migration across the electrode surface. Previous experimental work elsewhere has demonstrated the feasibility of this approach.[9]

The formation of etch pits in the surface of pure graphite flakes by catalyzed oxidation is well documented in the literature.[10-17] These studies demonstrated that when graphite is oxidized in the presence of a catalyst, characteristic patterns are formed in the graphite basal plane. These patterns depend on the catalyst[10-16] and on the gas.[11,17,18] For example, iron-oxide-catalyzed oxidation of graphite produces etch pits in the graphite basal plane,[11,12] whereas copper-oxide-catalyzed oxidation produces irregular channels in the graphite basal plane.[13]

In earlier work,[9] supports were prepared by the catalytic oxidation of graphite to a predetermined weight loss; then the supports were impregnated with high-surface-area platinum (100 m^2/g). Platinum sintering rates were measured as a function of time under conditions simulating the operation of phosphoric acid fuel cell cathodes. The results of this study demonstrate that the platinum sintering rate can be decreased by supporting the platinum on graphite that has been modified by catalytic oxidation with iron oxide. The purpose of the present program is to broaden the scope of this work by investigating 1) additional support materials, 2) alternative oxidation catalysts, and 3) extended sintering times up to 3000 hours.

EXPERIMENTAL STUDIES

Program Outline

This program has been divided into two phases, with each phase consisting of several tasks as outlined below.

Phase I. Support Modification

Task 1. Selection and Characterization of Carbon Supports

Task 2. Modification of Supports by Catalytic Oxidation

Task 3. Addition of Platinum to Support

Phase II. Sintering Studies

Task 4. Preliminary Sintering Studies

Task 5. Long-Term Sintering Studies.

In the following sections, the experimental studies performed will be described in the order given in this outline.

Task 1. Selection and Characterization of Carbon Supports

Three carbon supports were selected for investigation during the course of this work. They are 1) Vulcan XC-72R from the Cabot Corporation, 2) Vulcan XC-72 that has been graphitized by heating to 2500°C, and 3) Shawinigan acetylene black from the Shawinigan Products department of the Gulf Oil Chemical Company. Vulcan XC-72 is the most conductive furnace process carbon black produced by Cabot and is unique among carbon blacks in that it provides both high electrical conductivity and high surface area. The 2500°C graphitization performed on the Vulcan XC-72 by the Stackpole Corporation of St. Marys, Pennsylvania, increased the resistance of the carbon black to chemical oxidation, increased its electrical conductivity, and also lowered its surface area.

The third material, Shawinigan acetylene black, is formed by the thermal decomposition of acetylene gas at 800°C. It is a very pure form of finely divided carbon, which also exhibits good electrical conductivity. Table 1 lists some of the pertinent physical and chemical characteristics of the carbon supports.

Table 1. PHYSICAL AND CHEMICAL CHARACTERISTICS OF CARBON SUPPORTS

Support	Mean Particle Size, A	Purity, %	Surface Area (BET)*, m^2/g
Vulcan XC-72R	300	98	199
Vulcan SC-72/2500°C	--	99	77
Shawinigan AB	425	99.5	71

* As measured by IGT.

Task 2. Modification of Supports by Catalytic Oxidation

In the catalytic oxidation process, an aqueous solution of iron (III) formate or silver nitrate was added to the support under investigation in sufficient quantity, and of a concentration that, upon evaporation of the water, would provide a sample containing 0.1 wt % iron or silver. This mixture was evaporated to dryness in a vacuum oven at 150°C, agitated in a blender to decrease its bulk density, and placed in a 50-ml combustion boat. The boat was heated in a tube furnace under an argon atmosphere to a temperature between 550° and 800°C. This caused the decomposition of the metal salt to a metal oxide. An oxidizing gas, either oxygen or nitric oxide, was then added to the argon flow. After a period of time, the oxidizing gas was turned off and the sample cooled under an argon atmosphere. The boat was then removed from the furnace and weighed. The sample was then redistributed and the boat returned to the furnace. This procedure was repeated until the desired loss in weight was achieved. The final step in the modification procedure was to strip the catalyst from the carbon support. This was accomplished by washing the sample with 50% nitric acid followed by distilled water. The washed sample was dried for several hours in a vacuum oven at 150°C and stored under vacuum. Nitrogen adsorption isotherms were determined for the various samples using a Micromeritics Model 2100 D ORR Surface-Area Pore-Volume Analyzer. Table 2 lists the modification temperature, the time required to oxidize 1 wt % of the sample, and the final BET surface area of the sample.

The following alphanumeric code is used throughout this work to describe the origins of the various samples. The first letter of the sample designation indicates the starting material: V — Vulcan XC-72R, G — graphitized

Vulcan XC-72, and S — Shawinigan acetylene black. The chemical symbol, which is comprised of the second and third letters, represents the catalyst used to modify the sample: Fe — iron oxide, Ag — silver oxide. The fourth letter represents the oxidizing agent used: O — oxygen, N — nitric oxide. The numeric portion, which follows the four letters, indicates the approximate weight lost by the sample during modification. Therefore, GFeN-15 represents a sample of graphitized Vulcan XC-72 that has been oxidized to a 15% weight loss by using an iron oxide catalyst in a nitric oxide atmosphere.

Table 2. RESULTS OF MODIFICATION OF CARBON SUPPORTS

Sample Designation	BET Surface Area, m^2/g	Modification Temperature, °C	Time Required for 1% Weight Loss, min
VFeO-7	243	500	2.3
VFeO-15	294	500	2.3
VFeO-25	266	500	2.3
VAgO-15	265	500	4.0
VFeN-15	363	700	1.7
SFeO-7	93	600	1.7
SFeO-15	147	600	1.7
SFeO-25	124	600	1.7
SAgO-15	184	550	2.0
SFeN-15	92	700	4.7
GFeO-7	91	600	4.7
GFeO-15	91	600	4.7
GFeO-25	93	600	4.7
GAgO-15	91	600	3.0
GFeN-15	101	800	10

The time and temperature data indicate that Vulcan XC-72R is most susceptible to catalytic oxidation, whereas graphitized Vulcan XC-72 is most resistant, and that nitric oxide is less active as an oxidizing agent than oxygen. In two out of three of the supports, however, the highest surface-area change was achieved using nitric oxide. Little difference was observed between silver oxide and iron oxide, either as to the time-temperature data or to the final surface area achieved by modification.

An investigation of the acidity of the modified supports was also undertaken. It is known that the pH value of carbon black is related to the amount of carbon-oxygen complexes on the surface of the material and that furnace carbon blacks usually possess low concentrations of carbon-oxygen complexes

and, hence, exhibit slightly alkaline pH values. The pH of a carbon black can be determined with a standard glass electrode by making a carbon black-water slurry using degassed, distilled water. Table 3 lists the experimentally determined pH values for each of the three starting materials and for the three materials catalytically oxidized to a 15% weight loss under oxygen and under nitric oxide. It can be seen that there is a leveling effect under the strong oxidizing conditions encountered here. All oxidized samples show a final pH value of approximately 5, regardless of the origin of the original sample.

Table 3. pH VALUES OF VARIOUS CARBON SUPPORTS

Carbon Type	Oxidizing Agent	pH
Vulcan XC-72R	None	7.1
Vulcan XC-72R	Oxygen	5.0
Vulcan XC-72R	Nitric Oxide	4.7
Graphitized XC-72	None	8.4
Graphitized XC-72	Oxygen	5.1
Graphitized XC-72	Nitric Oxide	6.1
Shawinigan A.B.*	None	4.3
Shawinigan A.B.	Oxygen	5.0
Shawinigan A.B.	Nitric Oxide	5.5

* A.B. = acetylene black.

The purpose of this work, however, is not simply to increase the surface area of the supports, but to do so by creating micropores within the structure. Figure 1 is a representation of the nitrogen adsorption isotherm for sample GFeN-15. The pressure-volume data presented in the nitrogen adsorption isotherm can be used to construct a t-plot from which the success or failure of the modification procedure can be determined.[19-22]

In a t-plot analysis the t-value, which represents the assumed thickness of the adsorbed layer, is plotted versus the volume of nitrogen adsorbed as

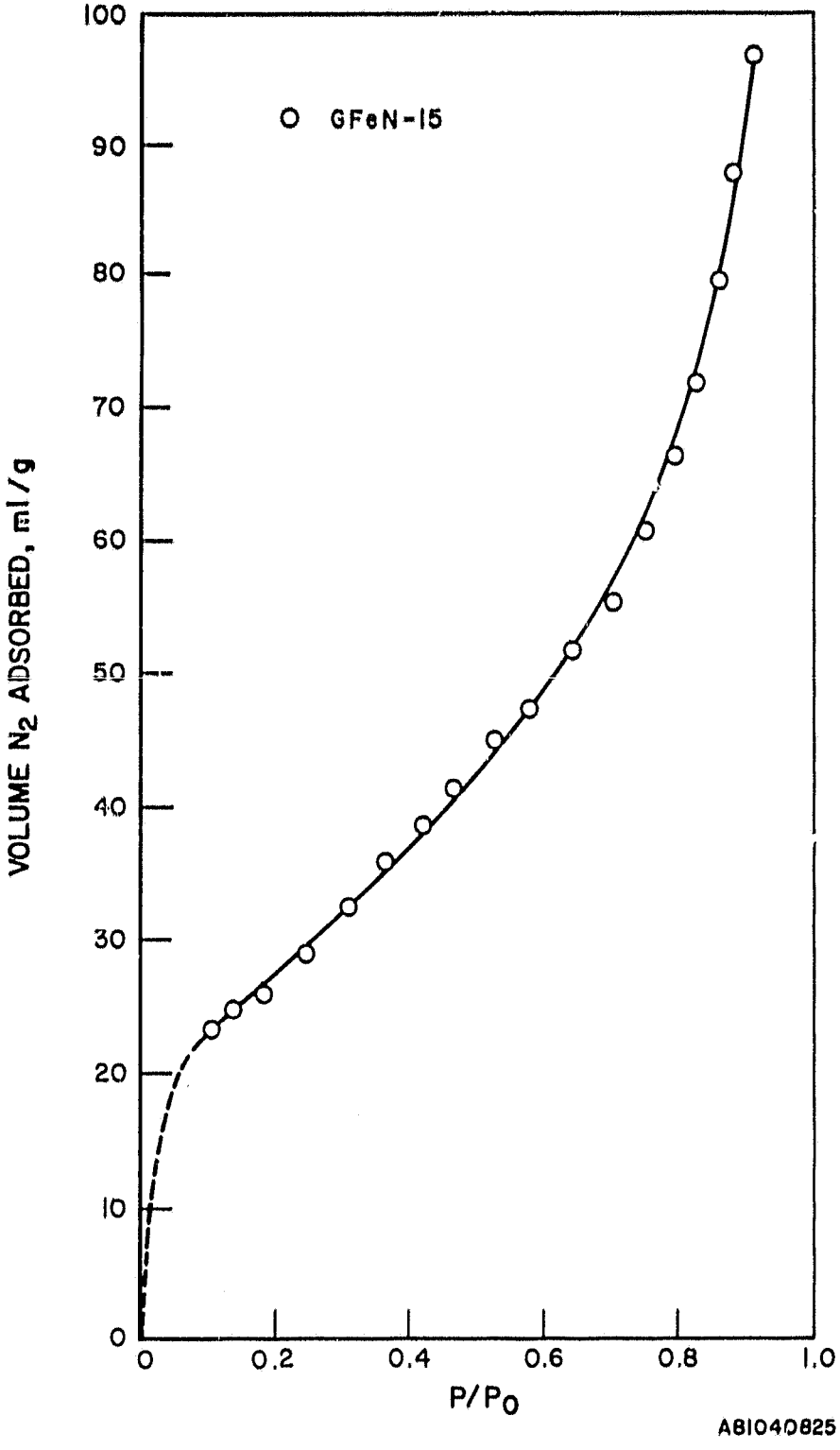

Figure 1. TYPICAL NITROGEN ADSORPTION ISOTHERM USED TO PROVIDE DATA FOR t-PLOT ANALYSIS

determined from the adsorption isotherm data. The t-value is itself a logarithmic function of the relative pressure P/P_0. The actual relationship between t and P/P_0 is determined experimentally, however. The t-values of Pierce[22] appear to be most useful in the present work.

There are three possible shapes for a V-t plot[21]:

1) If multilayer adsorption occurs on the surface of a nonporous material, the V-t plot is a straight line passing through the origin.

2) If, at some pressure, multilayer adsorption is augmented by capillary condensation in the pores of a porous material, the experimental points will deviate upward from the straight line.

3) If, on the other hand, a material contains narrow pores or slits with a large surface-to-volume ratio, the surface area of these pores will contribute to multilayer adsorption only up to pressures where t is of the same magnitude as the pore radius. Then they will be filled and cease to contribute. At this point the V-t plot will begin to deviate downward from a straight line.

Nonporous behavior is expected for graphitized carbon. Figure 2 illustrates that the t-plot of the unmodified graphitized Vulcan XC-72 does produce a straight line passing through the origin. The slight positive deviation of this t-plot at high relative pressures (t>10) can be attributed to capillary condensation of nitrogen in large mesopores[23] of diameters greater than 110 Å. The t-plots of the graphitized carbon samples that had been modified by catalytic oxidation also exhibit straight-line behavior in the regions where t is between 4 and 8. Nevertheless, these straight lines (Figures 2 and 3) do not extrapolate through the origins. Such behavior indicates that modification has produced a significant number of pores in shapes conducive to capillary condensation. Furthermore, this capillary condensation is already under way at a t-value of 4.5. Such behavior is consistent with pores of 10-Å and larger diameters.

The graphitized carbon samples modified by using an iron oxide catalyst in oxygen (GFeO-7, 15, and 25 in Figure 2) exhibit a remarkable straight-line behavior in this regard, whereas those treated with iron oxide in nitric oxide (GFeN-15) and with silver oxide in oxygen (GAgO-15) show some negative deviation at higher relative pressures (Figure 3). This suggests that, in the latter two samples, the pore sizes are limited to the range from 10 Å to 50 Å — an ideal size for trapping 40-Å-diameter platinum crystallites.

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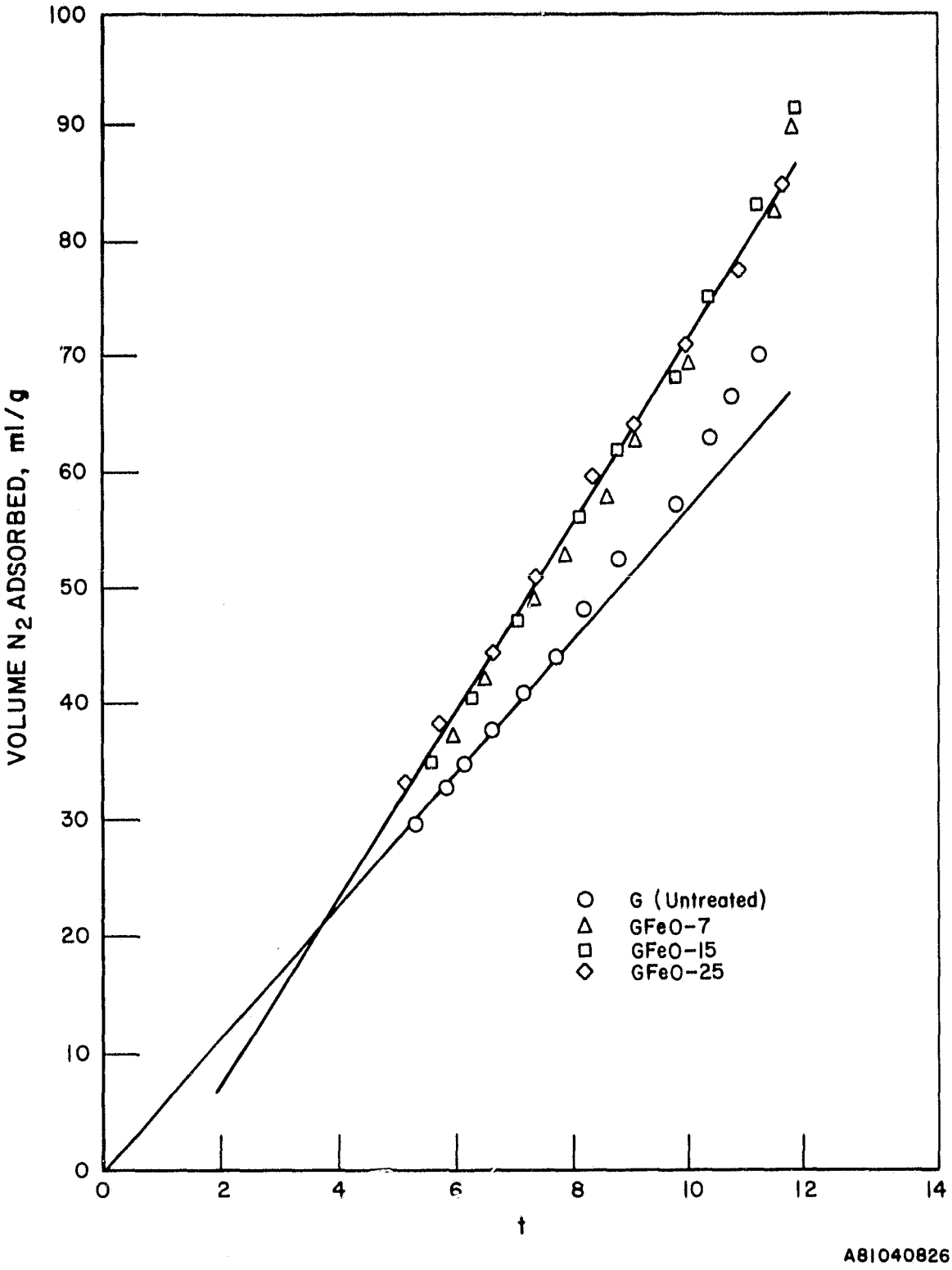

Figure 2. V-t PLOTS FOR UNTREATED GRAPHITIZED VULCAN XC-72 AND FOR SAMPLES CATALYTICALLY OXIDIZED WITH IRON OXIDE IN AN OXYGEN ATMOSPHERE

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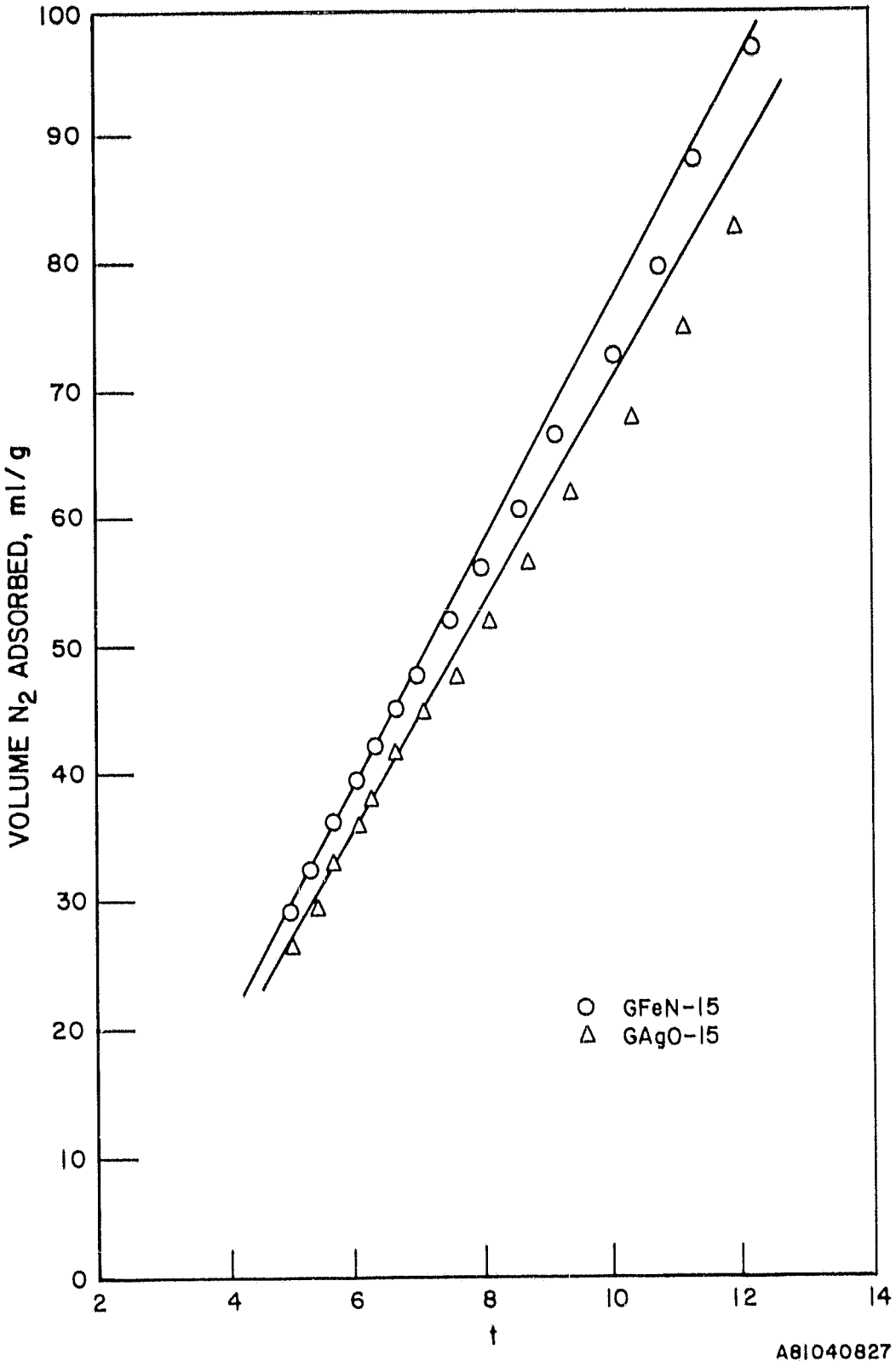

Figure 3. V-t PLOTS FOR SAMPLES OF GRAPHITIZED VULCAN XC-72 MODIFIED USING AN IRON OXIDE CATALYST IN NITRIC OXIDE AND A SILVER OXIDE CATALYST IN OXYGEN

Performing a t-plot analysis for the unreacted Shawinigan acetylene black (Figure 4) yields a change in slope, which occurs at an approximate t-value of 7. This suggests the presence of micropores with diameters less than 40 Å. As the V-t points above a t-value of 7 lie on a straight line passing through the origin, one can conclude that the micropores in the untreated Shawinigan are of a shape conducive to capillary condensation. The catalytic oxidation of the Shawinigan to a 7% weight loss increases surface area but does not appear to create new pores in doing so. On the other hand, the samples modified to a 15% or 25% weight loss (Figures 4 and 5) show a complex behavior indicating the presence of pores with shapes conducive to capillary condensation at t-values less than 6, and mesoslit pores with a high surface-to-volume ratio, which ceases tc contribute to the total surface area at t-values above 7. The t-plot of the modified sample designated SFeO-15 exhibits the greatest deviation from the t-plot of the unreacted Shawinigan and is reproduced in both Figures 4 and 5 for purposes of comparison.

The Vulcan XC-72R exhibits a behavior in Figure 6 that is considerably different from the behavior of the other two untreated supports. The t-plots of the untreated Vulcan as well as 4 of the 5 modified samples all yield straight lines that, when extrapolated to the volume axis, cross the t = 0 line at positive volumes. Behavior of this kind indicates materials possessing micropores that fill at very low relative pressures. It should be noted that capillary condensation can occur at pressures even below those required to form a monolayer on a free surface. The t-plots also indicate that the filling of these pores is already complete at a t-value of 4.0, which places the maximum diameter of these micropores at 10 Å. Pores of this size are of little use in the present program. Nevertheless, the t-plots of the samples catalyzed to a 15% weight loss (Figures 6 and 7) also indicate the formation of mesoslits or micropores having a diameter of 40 Å or less. Particularly interesting behavior is exhibited by the sample oxidized with nitric oxide (VFeN-15). Here the low-pressure points of the V-t plot lie on a straight line passing through the origin, indicating that the micropores of diameters less than 10 Å have either been collapsed or altered in size. The sharp change in the slope of the line at a t-value of 7 indicates the presence of relatively uniform pores having a maximum diameter of 40 Å. It should be recalled from Table 2, however, that because of the low oxidation rate observed with nitric oxide relative to oxygen, the modification procedures

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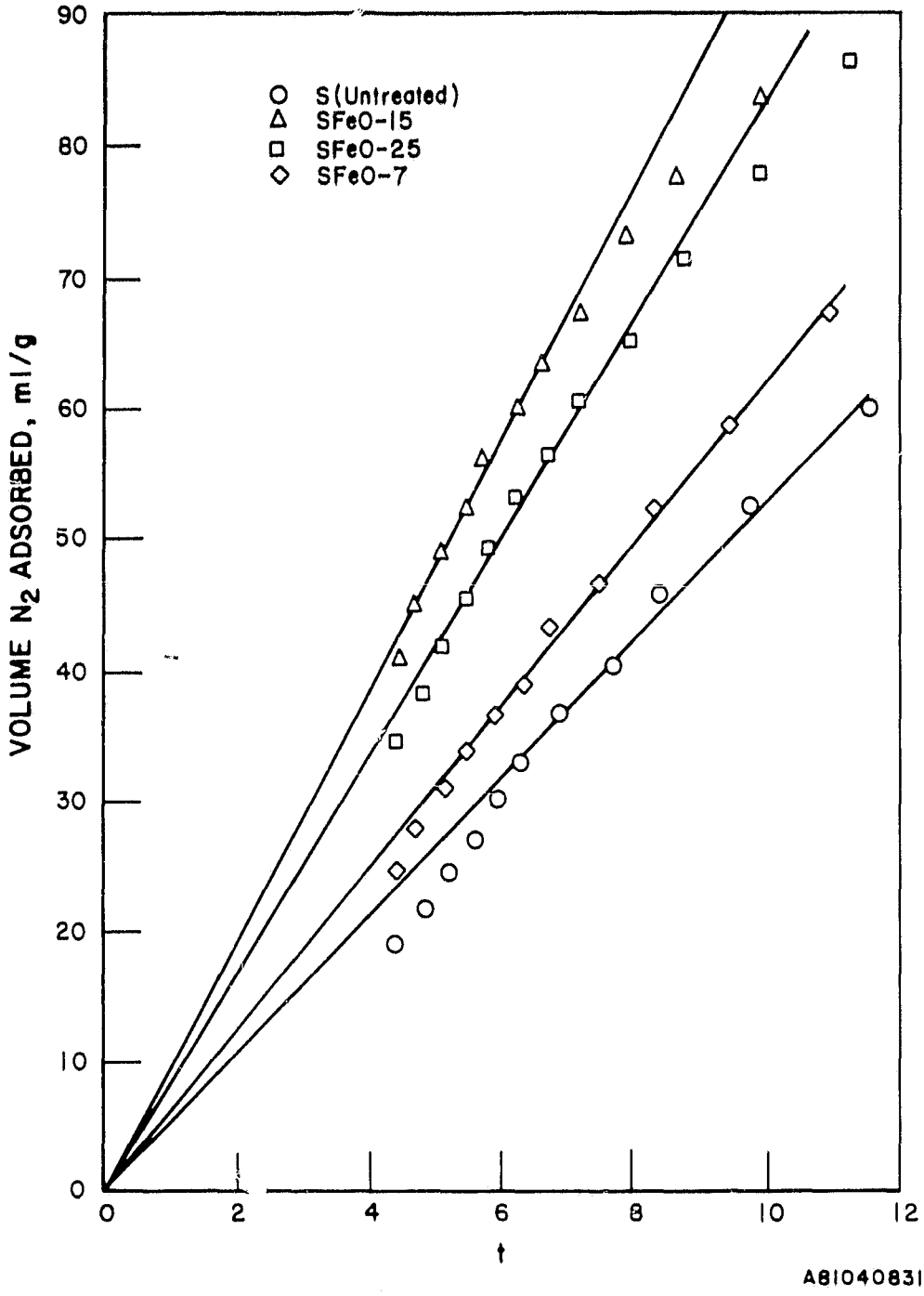

Figure 4. V-t PLOTS FOR UNTREATED SHAWINIGAN ACETYLENE BLACK AND FOR SAMPLES CATALYTICALLY OXIDIZED WITH IRON OXIDE IN AN OXYGEN ATMOSPHERE

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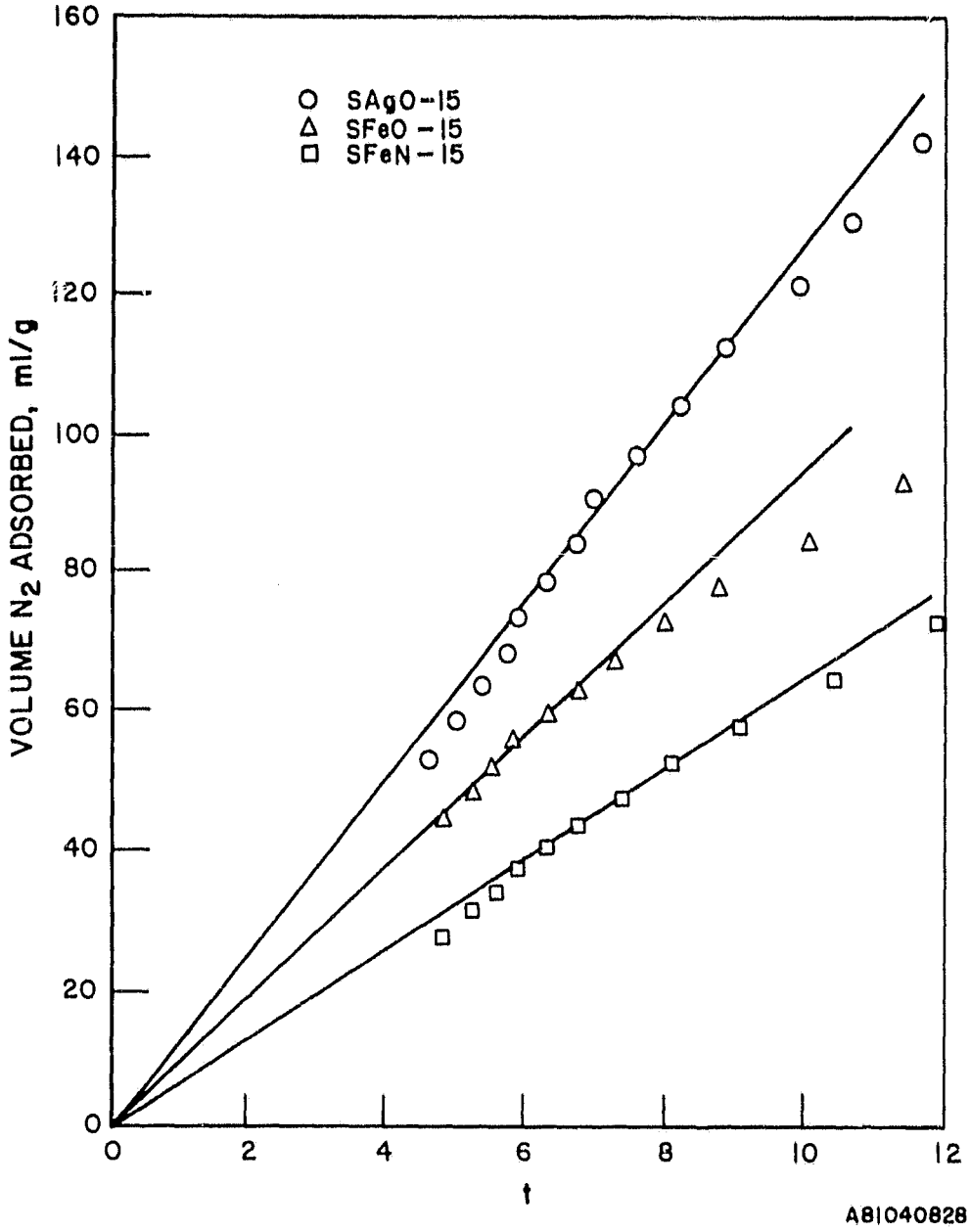

Figure 5. V-t PLOTS FOR SAMPLES OF SHAWINIGAN ACETYLENE BLACK THAT HAVE BEEN CATALYTICALLY OXIDIZED TO A 15% WEIGHT LOSS USING VARIOUS MEANS

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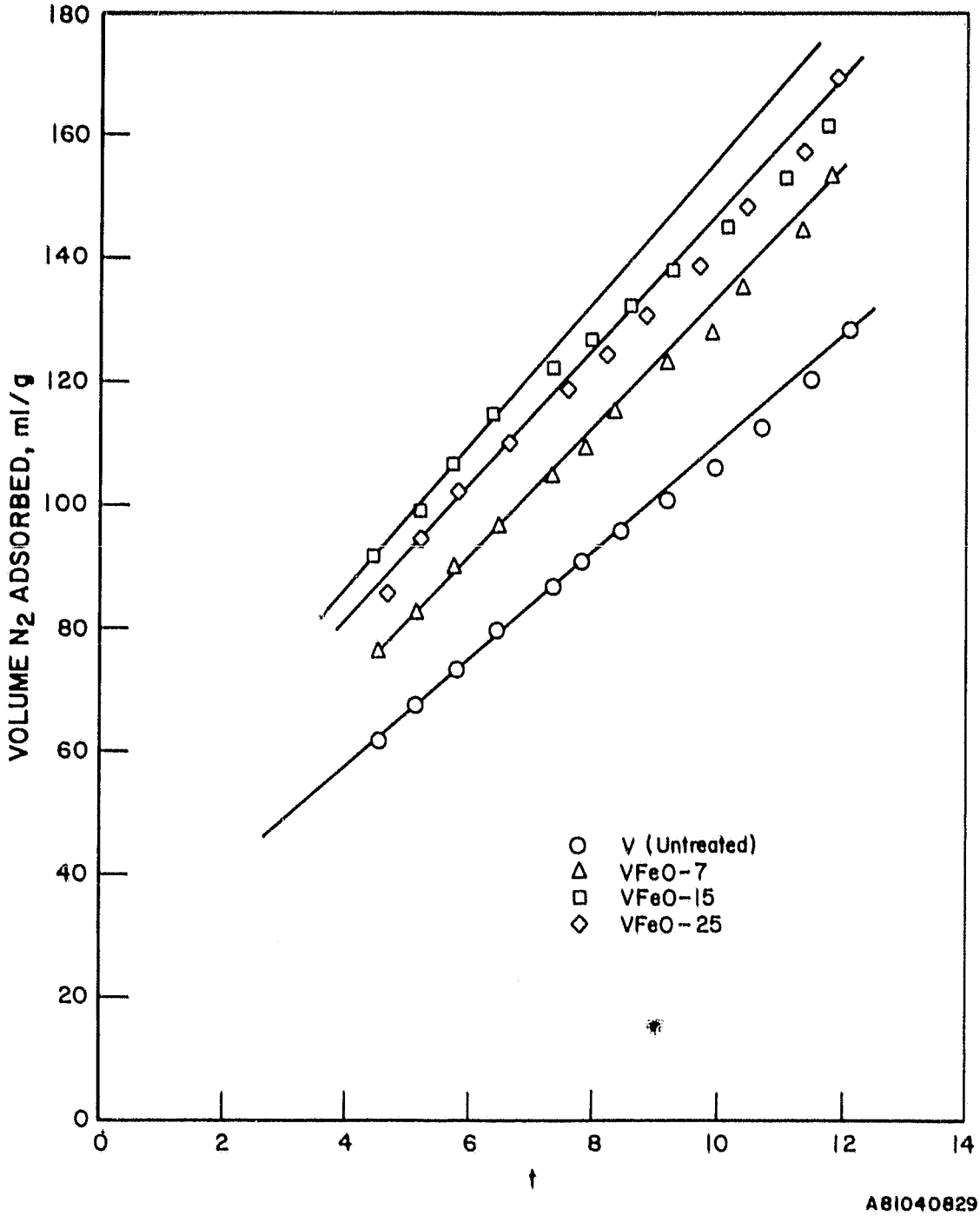

Figure 6. V-t PLOTS FOR UNTREATED VULCAN XC-72R AND FOR SAMPLES CATALYTICALLY OXIDIZED WITH IRON OXIDE IN AN OXYGEN ATMOSPHERE

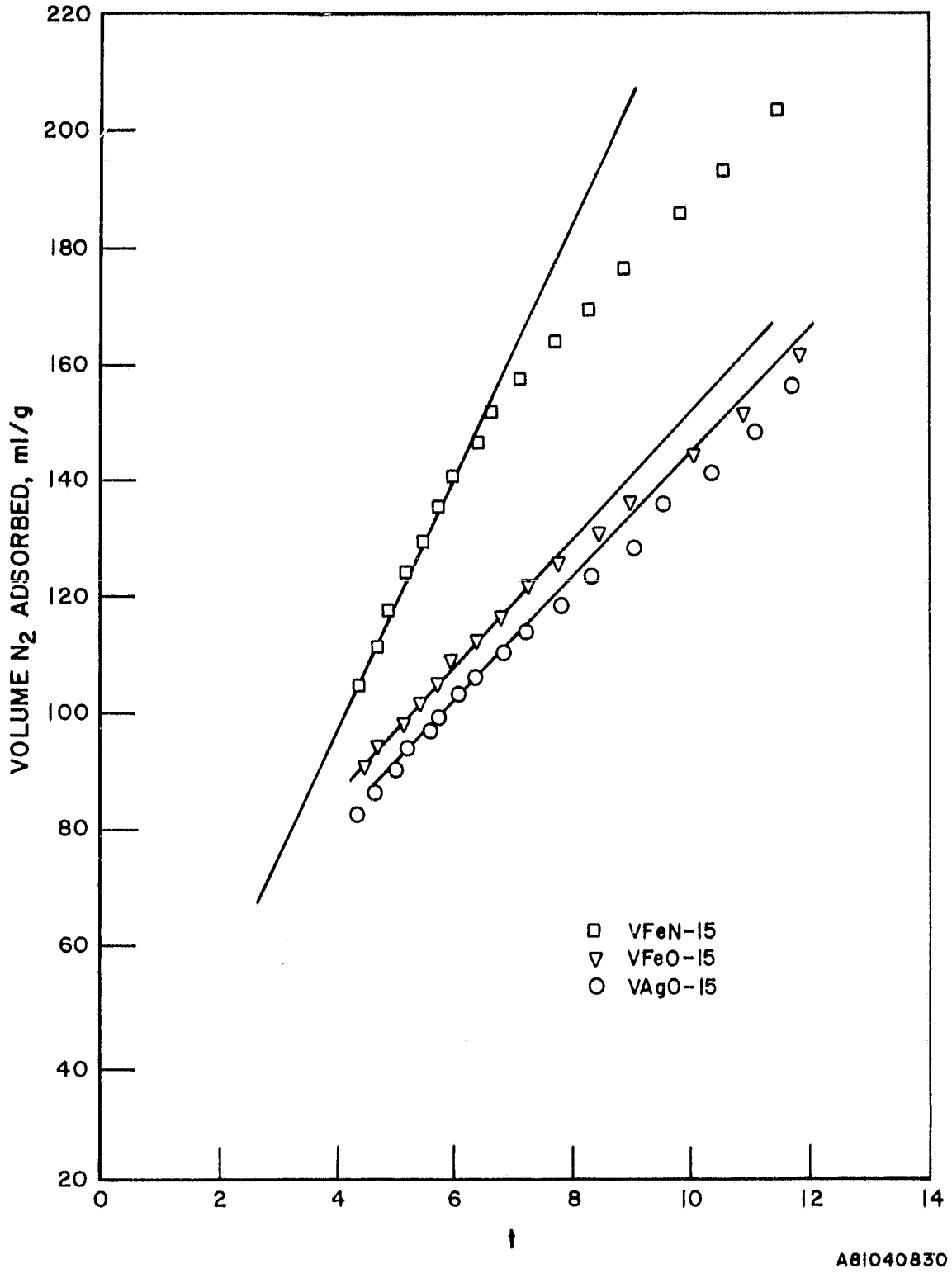

Figure 7. V-t PLOTS FOR SAMPLES OF VULCAN XC-72R THAT HAVE BEEN CATALYTICALLY OXIDIZED TO A 15% WEIGHT LOSS USING VARIOUS MEANS

using this agent had to be performed at higher temperatures to complete an experiment in a reasonable time period. Thus, sample VFeN-15 was modified at 700°C, whereas the remaining samples were modified at only 500°C. It is possible that this higher temperature, rather than the nitric oxide, is responsible for the change in structure of the material.

This possibility was investigated by powder-pattern X-ray diffraction analysis on samples of untreated Vulcan XC-72R, the modified support VFeN-15, and Vulcan XC-72 that had been graphitized at 2500°C.

In graphitic carbons, graphite-like layers are grouped in packets. Within these packets there is a random distribution of oriented and disoriented layers.[24,25] The reflection angle for the interlayer spacing for these graphite-like layers was chosen as a tool to investigate these three samples. When Vulcan XC-72R was examined by X-ray diffraction, a relatively small and narrow peak was observed that corresponded to an interlayer spacing of 3.38 Å. This is quite close to the interlayer spacing observed with pure graphite (3.354 Å). The sample of VFeN-15 exhibited a peak of slightly higher intensity than its starting material (Vulcan XC-72R), and the peak was shifted slightly toward a higher interlayer spacing of 3.40 Å. The sample of Vulcan XC-72 that had been graphitized at 2500°C exhibited a very broad and intense peak. The peak maximum occurred at a reflection angle that corresponded to an interlayer spacing of 3.48 Å. The results are summarized below:

Sample	Interlayer Spacing, Å	Relative Peak Intensity
Vulcan XC-72R	3.38	1.0
VFeN-15	3.40	1.6
Vulcan (2500°C)	3.48	17.4

Changes in both interlayer spacing, peak intensity, and width can be rationalized as follows: When a furnace black such as Vulcan XC-72R is examined by X-ray diffraction, a relatively narrow peak of low intensity is observed for the interlayer reflection because only a small percentage of the carbon in the sample is contained in graphite crystallites. These crystallites are small, but exhibit an interlayer spacing close to that of pure graphite. As the sample is heated, crystallite growth occurs by the gradual

displacement of whole layer-planes or even groups of layer-planes, and the intensity of the interlayer spacing peak in the X-ray increases. Because of cross-linking between neighboring crystallites and their originally random orientation, however, the growing crystal exhibits slightly greater than ideal interlayer spacing ranging anywhere from 3.354 A to 3.7 A. The original starting material contained only a small number of highly perfect planar graphite-like layers. The bulk of the sample was much less organized and gave only gas-like contribution to the X-ray scattering. Therefore, additional contributions of the newly formed less-than-perfect layers to the X-ray scattering caused the interlayer spacing reflection to both increase in intensity and broaden in the direction of larger spacing distances. The results indicate that some minor graphitization has taken place during the preparation of modified sample VFeN-15, but that the degree of graphitization is insufficient to explain the large changes in physical characteristics observed during the modification procedure. Thus one must assume that the oxidization process using nitric oxide contributed heavily to the restructuring of sample VFeN-15.

Task 3. Addition of Platinum to Supports

At the completion of Task 3, 18 separate and distinct carbon supports had been prepared. Tables 1 and 2 list these 18 supports with their BET surface areas.

Of the 18 supports, 10 were chosen for further investigation in Task 3 and Task 4 work. Seven of these were selected on the basis of the pore structure analysis performed in Task 2, which indicated that these 7 supports underwent an extensive structural modification of the type consistent with the formation of etch pits. In addition, three samples (one from each unmodified support listed in Table 1) were carried over into Task 3 to act as controls.

All 10 of these supports were impregnated with platinum through a procedure similar to one that is described by Cairns[26]: Identical 500-mg samples of each of the 10 supports were placed in separate glass containers. Four milliliters of a 50 vol % nitric acid solution containing sufficient diamino platinum (II) dinitrite (DPN) to provide 50 mg of platinum metal were added to each container. All 10 containers were then placed in an oven and heated in a stepwise manner. Table 4 lists the temperature plateaus and the length of time that each temperature was maintained.

Table 4. TIME-TEMPERATURE PROGRAM FOR THERMAL DECOMPOSITION OF PLATINUM SALT

Temperature, °C	Time, min
82	45
90	90
115	160
135	980
215	240

An 11th sample was prepared under an inert atmosphere, using 500 mg of support material GFeO-15. Using a glazed combustion boat, a slurry was prepared by adding 4 ml of the DPN-containing solution. The boat was placed in a vacuum oven and the time-temperature program was run, under a vacuum of less than 1 torr, up to the end of the 135°C plateau. The boat was then cooled to room temperature under vacuum, removed from the vacuum oven, and placed in a tube furnace. After purging the tube furnace for 1 hour with ultrahigh-purity (UHP) nitrogen (better than 99.999% purity), the sample was heated at 235°C for 4 hours and the platinum compound was decomposed under a steady nitrogen flow. The sample was then cooled and exposed to air. This 11th sample carries the designation GFeO-15-DPN-Inert.

A 12th and final sample was catalyzed by impregnation with colloidal platinum. The modified carbon support designated GFeO-15 was again used as the starting material. The following procedure was used to catalyze this sample: A solution was prepared by adding 20 ml of a 0.04-molar sodium citrate solution and 15 ml of a 0.0077-molar chloroplatinic acid solution to 135 ml of deionized water. This mixture was heated for 18 hours at 95°C in a 500-ml flask fitted with a condenser. During this period the sodium citrate reduced the chloroplatinic acid to form a colloidal suspension, or "sol," of platinum metal. The optical absorbance of this material was measured periodically with a Bausch & Lomb Spectronic 21 spectrophotometer indexed to a wavelength of 450 nm.

After 18 hours, the slowly increasing absorbance had leveled off at 0.87, indicating that the reaction had ceased. The platinum sol was then filtered

through a 0.45-micron cellulose nitrate membrane and a 47-mm millipore vacuum filtration apparatus packed with Amberlite MB-3 ion exchange resin. The absorbance of this deionized sol was measured and determined to be 0.85 at 450 nm, indicating that most of the platinum had survived the deionization procedure. Four drops of a 1% silver nitrate solution were then added to 2 ml of the sol as a test for residual chloride; the test indicated that no chloride was present. The final volume of solution was 155 ml, indicating that 15 ml of the original 170 ml had been retained by the ion exchange resin. Precisely 200 mg of the GFeO-15 carbon support were then added to the 155 ml of platinum sol, and the mixture was agitated in a glass-lined ultrasonic bath for 3 hours. The suspension was transferred to a drying oven and evaporated to dryness at 90°C over a 48-hour period. This 12th sample carries the designation GFeO-15-Colloidal.

A chemical analysis was performed on a portion of selected samples of the catalyzed supports. The results indicated that the 10 supports that underwent impregnation by DPN decomposition in air contained about 5 wt % platinum. The 11th sample, which was catalyzed by vacuum evaporation and DPN decomposition in an inert atmosphere, contained 7 wt % platinum, and the sample to which colloidal platinum had been added contained 8 wt % platinum. The initial starting materials in all cases were sufficiently rich in platinum to produce a maximum loading of 10 wt %. Deposits of significant quantities of platinum were observed on container walls, however; this accounts for the differences.

Four of the platinum-catalyzed supports were examined by transmission electron microscopy (TEM) by the Small Particles Research Group of the Illinois Institute of Technology Research Institute (IITRI). These four materials were unmodified graphitized Vulcan XC-72 (G), graphitized Vulcan XC-72 that had been modified by catalytic oxidation to a 15% weight loss using an iron oxide catalyst in an oxygen/argon atmosphere at 600°C (GFeO-15), Shawinigan acetylene black that had been modified in the same manner (SFeO-15), and Vulcan XC-72R that had been catalytically oxidized to a 15% weight loss using an iron oxide catalyst in a nitric oxide/argon atmosphere at 700°C (VFeN-15).

Figures 8 through 11 represent the best TEM's obtained while operating the instrument at its highest resolution. Figures 8, 9, and 10 show that the platinum crystallites (dark spots) residing on the supports are of a finely

Figure 8. ELECTRON MICROGRAPH OF 5% PLATINUM ON GRAPHITIZED VULCAN XC-72

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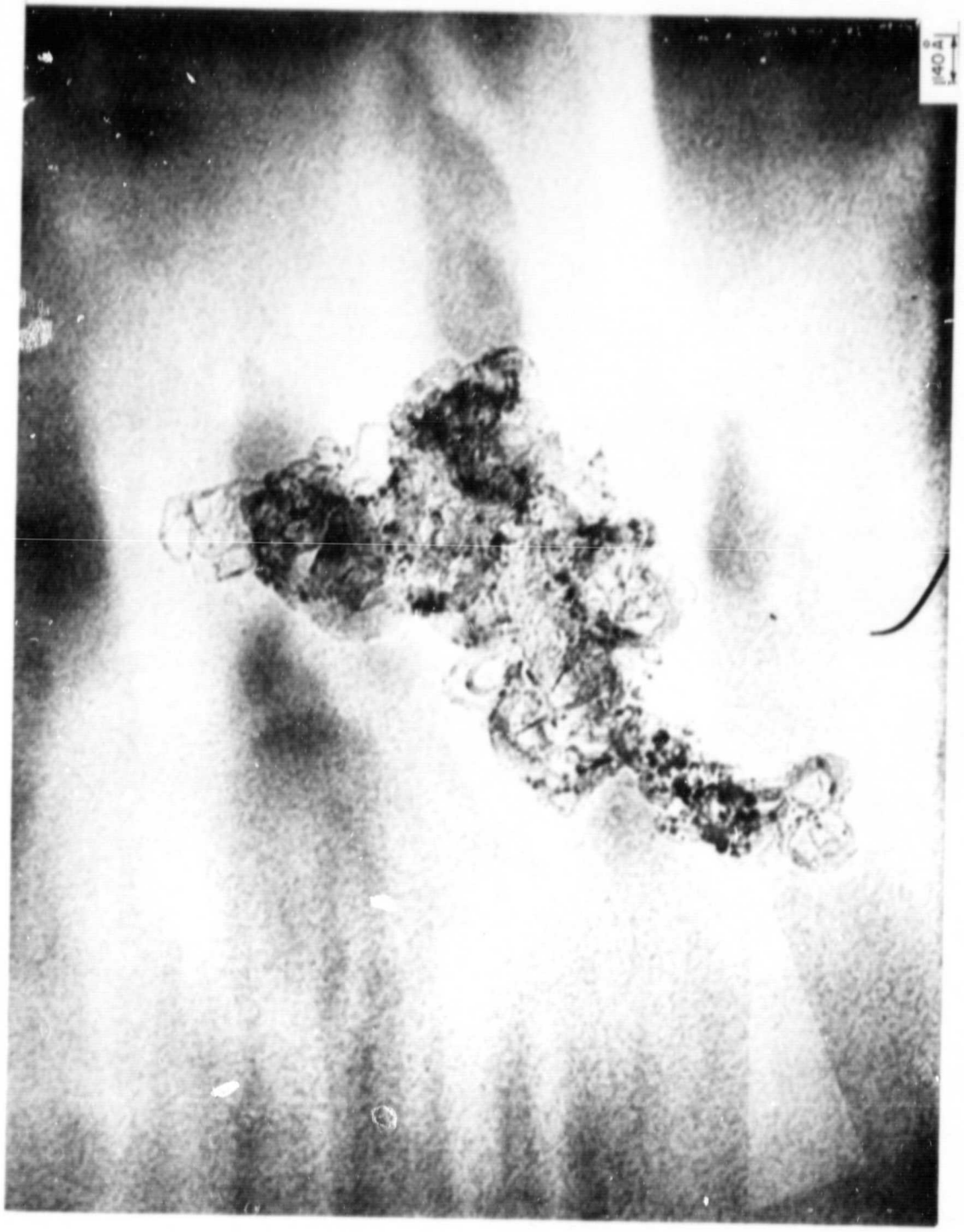

Figure 9. ELECTRON MICROGRAPH OF 5% PLATINUM ON SUPPORT GFeO-15

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Figure 10. ELECTRON MICROGRAPH OF 5% PLATINUM ON SUPPORT SFeO-15

divided nature with particle diameters on the order of 25 Å to 40 Å. This is consistent with specific surface areas on the order of 50 to 100 m^2 per gram of platinum. Figure 11, however, shows no black areas indicative of platinum crystallites. Repeated attempts to prepare samples of this material exhibiting the dark areas met with failure. This result is puzzling because this material proved to have excellent activity as an oxygen reduction catalyst in the phosphoric acid environment. There are two possible explanations for the absence of platinum crystallites in the TEM of VFeN-15: 1) The technique used to prepare the four supports for TEM analysis failed to yield representative samples for VFeN-15, or 2) the diameter of the platinum crystallites supported on VFeN-15 is less than the resolution of the instrument.

Task 4. Preliminary Sintering Studies

The following procedures were used to evaluate Teflon-bonded test electrodes for preliminary catalyst sintering-rate studies.

Electrode Fabrication

Fifty milligrams of supported catalyst prepared in Task 3 were placed in a 5-ml beaker and wetted with 2 to 4 drops of deionized water. A water dispersion of Teflon-30 was then added in sufficient quantity to provide approximately 10 weight percent of Teflon solids in the final dried composite. These materials were mixed thoroughly, and the wet composite, which had the consistency of putty, was spread uniformly onto a platinum screen, using firm pressure on a hand-held spatula.

The electrode was dried at 95°C for 30 minutes and the composite firmly pressed a second time with the spatula. The electrode was then heated in an oven at 330°C for 15 minutes to drive off all dispersing agents and sinter the Teflon. The electrode was then removed and pressed between two aluminum foil platens heated to approximately 250°C. The pressing time was about 3 minutes at 500 lb on the 1/4-in.^{2} (1.4-cm^2) electrode.

The finished electrode was then weighed to obtain an estimate of catalyst loading.

Surface-Area Measurements

The platinum surface areas of the 12 test electrodes prepared by the above procedure were measured both before and after a 24-hour sintering test

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Figure 11. ELECTRON MICROGRAPH OF 5% PLATINUM ON SUPPORT VFeN-15

using triangular-potential sweep-cyclic voltammetry. In this procedure, a continuous triangular wave is supplied by a Wavetek Model 185 sweep generator and fed to the input side of an Amel Model 549 potentiostat. The voltage of the test electrode was monitored versus a saturated calomel reference electrode (SCE) with a Keithley 616 digital electrometer, and the cyclic voltammogram was recorded on a Hewlett-Packard Model 7035B X-Y recorder. The surface area of the platinum supported on the carbon was calculated by integrating that portion of the current voltage curve of the cyclic voltammogram associated with the oxidation of adsorbed hydrogen. The following equation was used to relate the charge required to oxidize the adsorbed hydrogen to the surface area of the supported platinum catalyst[27]:

$$\text{Pt surface area } (m^2/g) = \frac{0.476\ (m^2/A\text{-}s) \times \text{charge } (A\text{-}s)}{\text{Pt loading of the electrode in grams}}$$

Preliminary tests indicated that the optimum conditions for obtaining a reproducible surface-area measurement using this electrochemical method included pretreatment of the test electrode in hot (150°C) phosphoric acid (85%) for 12 hours before the first surface-area determination. Pretreatment was accomplished in an open beaker with no electrical connections to the test electrode. After pretreatment in phosphoric acid, the electrode was washed in deionized water and placed in 4N H_2SO_4 electrolyte at room temperature adjacent to a saturated calomel electrode and opposite a platinum counterelectrode. The electrolyte was sparged for 30 minutes with argon to eliminate any dissolved oxygen and then connected to the potentiostat. The sweep generator was engaged and the electrode was "cycled" for several minutes between the two voltage extremes at —180 and +1350 mV versus the SCE at a rate of 200 mV/s. An independent measurement indicated that the SCE electrodes used with this apparatus were at a potential +191 mV positive of reversible hydrogen in this electrolyte. Therefore, the test electrode approached within 10 mV but at no time reached the reversible hydrogen potential where hydrogen gas evolution becomes significant. After scanning at 200 mV/s for several minutes to clean the electrode, the rate was slowed to 20 mV/s, and a preliminary cyclic voltammogram was taken for purposes of identifying possible contamination. The standard reduction potential of both silver (I) and iron (III) fall in the range of +450 to +600 mV versus SCE, and if any metal oxide catalyst remained in the support, it would have been obvious at this point.

If the preliminary cyclic voltammogram indicated that all electronics were adjusted correctly and no contaminants were present, the scanning rate was adjusted to 2 mV/s and a cyclic voltammogram recorded under an argon atmosphere. The electrode was then washed and a 24-hour sintering test performed. When the sintering test was completed, the electrochemical surface-area determination procedure was repeated, beginning with the deionized water wash. At the completion of this second, or "after," cyclic voltammogram, the potentiostat was disengaged and the sparging gas changed from argon to carbon monoxide. After sparging with carbon monoxide for 60 minutes, a triangular-potential sweep voltammogram was run, beginning at +250 mV versus SCE, scanning at 2 mV/s in the negative direction to —180 mV, and moving back in the positive direction to +600 mV versus SCE. The purpose of this procedure was to obtain a background scan of the important adsorbed hydrogen region under conditions where the hydrogen adsorption was blocked by adsorbed carbon monoxide. The differences between scans performed under carbon monoxide and under argon in the important potential region between —180 and +250 mV (SCE) provide the information required to calculate the surface area of the platinum. A typical cyclic voltammetric study is illustrated in Figure 12.

Sintering Test Procedure

After the initial determination of platinum surface area, the electrode was washed with copious amounts of deionized water and gently dried in a vacuum oven with a slowly decreasing pressure. The test electrode was then plunged into a 300-ml reservoir of 100% phosphoric acid maintained at 191°C. The vacuum drying was found to be necessary to prevent steam explosion of the porous electrode upon immersion in the hot acid. Moreover, because recent work by Stonehart Associates, Inc.,[28] has indicated a positive relationship between water vapor pressure and the corrosion rate of carbon supports in concentrated acid and, further, that the rate is highest during the first hour of operation, it was deemed inadvisable to begin with a wet electrode in cold acid and heat up to temperature.

A reversible hydrogen electrode (RHE) fitted with a Luggin capillary and its own separate gas supply was immersed in the phosphoric acid reservoir and used as a reference electrode. The sintering tests were performed with a platinum counterelectrode, and an inert argon atmosphere was maintained at the proper water vapor pressure with an in-line humidifier. The test electrode

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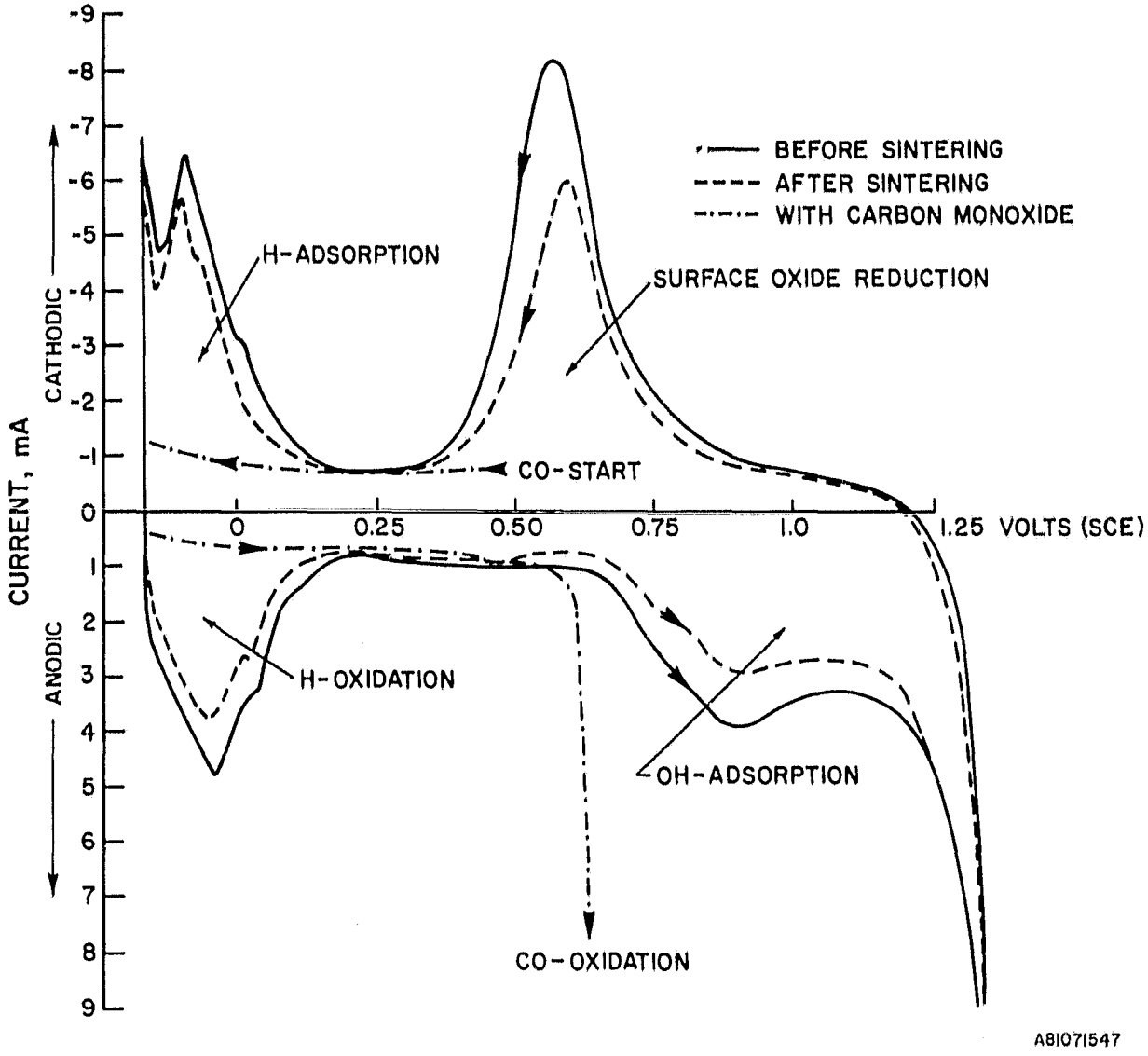

Figure 12. CYCLIC VOLTAMMOGRAM OF ELECTRODE GFeO-15-COLLOIDAL AT A SCAN RATE OF 2 mV/s. (The Loss of Platinum Surface Area Due to Sintering is Evident in Four Separate Regions. Of These, the Region Associated With the Oxidation of Adsorbed Hydrogen is Most Reproducible.)

was potentiostatted for 24 hours at a potential +650 mV positive of the RHE, and slow stirring of the electrolyte was accomplished with a Teflon stir-bar located immediately below the test electrode.

Although the static, flooded-electrode test conditions are somewhat removed from the operating conditions of a dynamic, gas-diffusion electrode in a phosphoric acid fuel cell, catalyst sintering studies performed by Pan et al.[29] at Exxon Corp. indicate that these conditions provide a useful accelerated sintering test with results representative of sintering in actual fuel cells.

Results of 24-Hour Static Tests

Table 5, a brief summary of the sintering results by sample designation, lists both the "before" and "after" active surface areas of the platinum catalysts and the percentage loss in surface area after the 24-hour static test.

Table 5. SUMMARY OF RESULTS FROM 24-HOUR SINTERING STUDIES

Sample Designation	Platinum-Specific Surface Area, m^2/g		
	Before	After	Loss, %
G (Unmodified)-DPN-Air	78	50	36
GFeO-15-DPN-Air	67	33	51
GFeO-15-DPN-N_2	49	38	23
GFeO-15-Colloidal	73	50	31
GAgO-15-DPN-Air	65	38	41
S (Unmodified)-DPN-Air	42	21	50
SFeO-15-DPN-Air	98	53	46
SFeO-25-DPN-Air	59	40	32
SAgO-15-DPN-Air	67	49	27
V (Unmodified)-DPN-Air	74	53	28
VAgO-15-DPN-Air	71	56	21
VFeN-15-DPN-Air (First Trial)	51	41	12
VFeN-15-DPN-Air (Second Trial)	41	37	10

1000-Hour Sintering Tests

Following completion of the 24-hour sintering tests, three of the modified supports, one from each of the three catagories of starting material, and unmodified, graphitized Vulcan XC-72 were used to fabricate gas diffusion electrodes. Figure 13 is a flow diagram summarizing the process used for support modification, impregnation, and fabrication of fuel cell electrodes. The modification and impregnation procedures are as described above in Task 2 and Task 3, respectively.

Following impregnation, the catalyzed supports were mixed with Teflon-30 to form a composite that was 10 wt % Teflon solids, 85 wt % carbon, and 5 to 7 wt % platinum. Sufficient water was added to give the composite the consistency of wet putty, and the mixture was then spread uniformly over one side of a carbon paper square obtained from the Stackpole Corporation. The reverse side of this square was lightly painted with Teflon-30; and the structure was dried at 75°C, heated to sinter the Teflon agglomerates at 330°C for 15 minutes, and pressed at 500 psi (35 kg/cm^2) for 10 minutes. A gold-coated tantalum screen was placed against the reverse side of the carbon paper to serve as a current collector, and a complete fuel cell was assembled using two such structures as gas diffusion electrodes. Catalyst loading on these electrodes was approximately 0.5 mg of platinum per cm^2. The frontal area of the electrode was 4 cm^2.

These fuel cells were operated at 191°C on air and hydrogen in a constant-voltage mode such that the air electrode was at a potential 650 mV positive of RHE.

After 24, 200, 500, and 1000 hours of operation, the phosphoric acid was drained from the fuel cell and replaced with 4M H_2SO_4. An electrochemical surface-area determination (ESAD) was then performed on the cathode, using triangular-potential sweep-cyclic voltammetry for the purpose of determining the platinum surface area and monitoring the rate of platinum sintering. Fuel cell cathodes were constructed for 1000-hour tests, using three of the modified supports — GFeO-15, SFeO-15, and VFeN-15 — and unmodified graphitized Vulcan XC-72. The latter material has become somewhat of an accepted standard in this type of research and is used here as a control. A fifth catalyzed support was prepared with GFeO-15 as a starting material. This modified support was impregnated with platinum and then treated by a procedure similar to one

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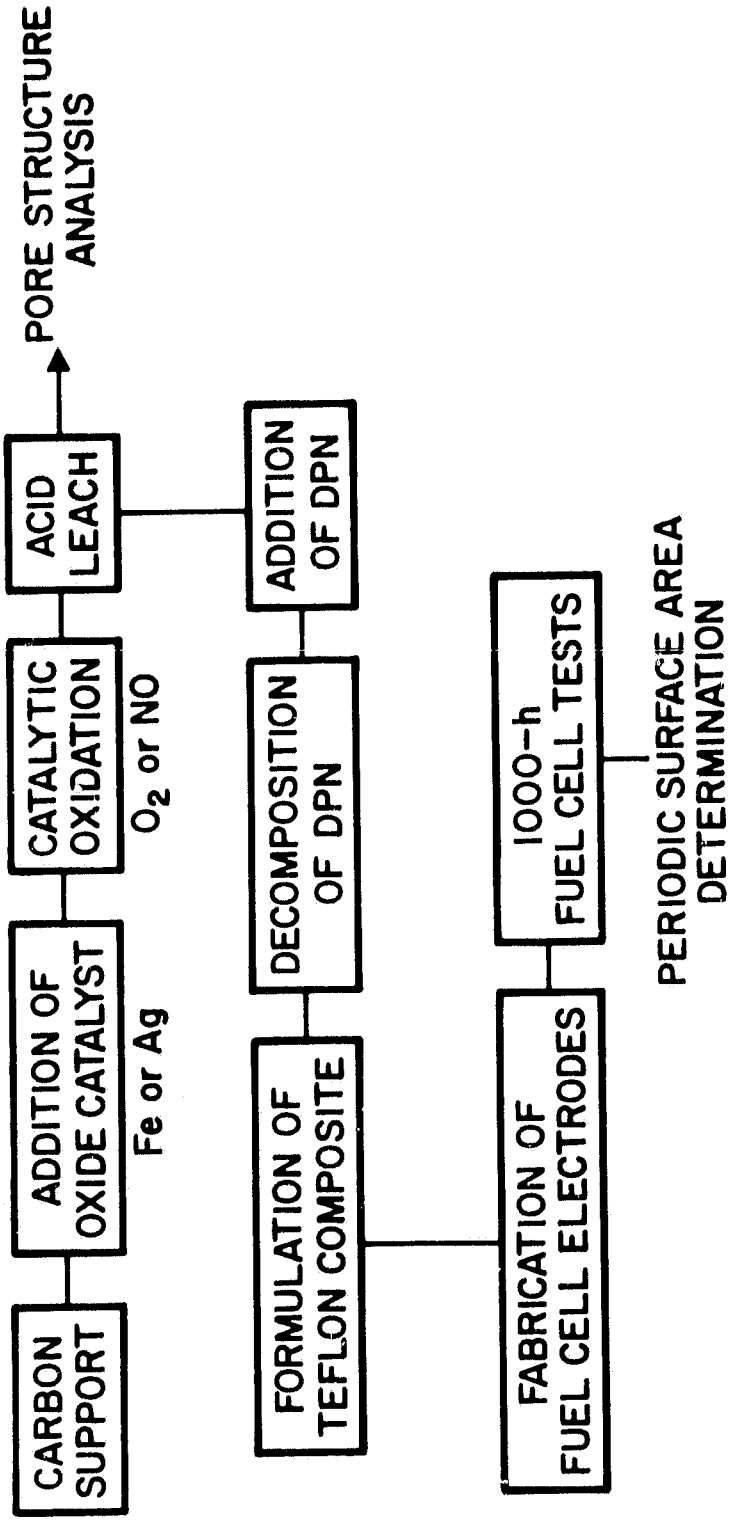

Figure 13. FLOW SHEET FOR THE PREPARATION OF PHOSPHORIC ACID FUEL CELL ELECTRODES

described by V. M. Jalan.[30] The support was placed in a tube furnace and warmed to 260°C under a carbon monoxide atmosphere. The sample was maintained at this temperature for 60 minutes and then cooled. This treatment procedure is presumed to cause carbon monoxide to disproportionate on the platinum crystallites according to the equation —

$$2CO \xrightarrow{Pt} C + CO_2 \qquad (1)$$

This presumption is at least partially supported by the fact that the total sample weight increases by several percent during treatment. The treated support was then reheated to 1000°C under an argon atmosphere to graphitize the carbon. This graphitization is necessary because it has been shown by others[28] that amorphous carbon is more susceptible to oxidation in the phosphoric acid environment than is graphitized carbon.

It is thought that heat-treating the catalysts in carbon monoxide achieves the same final result as the etch-pit procedure in that the platinum crystallites are contained in carbon cavities. In the latter process, a cavity is created by etching a pit into the graphite basal plane, whereas in the former, the cavity is formed by carbon deposition around individual catalyst particles. This fifth catalyst incorporates both techniques by impregnating an etched carbon support with platinum crystallites and then heat-treating the catalyzed support in a carbon monoxide atmosphere.

The designations used to distinguish the five catalyzed supports in the 1000-hour sintering tests are GFeO-15, SFeO-15, VFeN-15, G (unmodified), and GFeO-15-CO.

Evaluative Techniques

Three independent techniques are available for assessing the success or failure of these methods in preventing platinum crystallite sintering. One is to maintain the test electrode at a constant potential versus a reference in an operating fuel cell and to monitor the current flow as a function of time. Although the information gained from this technique bears directly on cell lifetime determination, it is not without ambiguities, as factors other than platinum sintering can influence performance.

A second technique of some value is the measurement of catalyst surface area by electrochemical methods, for example, the ESAD procedure previously

described. This technique provides a method of measuring the active surface area of a catalyst directly and is related to cell performance. Several factors besides catalyst sintering can contribute to surface-area loss, however — for example, (1) dissolution of the catalyst, (2) dislodgment of catalyst particles as a result of mechanical vibration or support corrosion, and (3) loss of electrical contact with catalyst particles as a result of mechanical failure on a microscopic level. In addition, several factors may be at work that can cause an increase in both performance and ESAD values with time. These include (1) favorable changes in the wettability of the Teflon-bonded catalyst layer; (2) movement of platinum crystallites from areas of poor electrical contact to areas of good contact, a process that would be expected if sintering rate were in fact a function of cathode potential; and finally (3) the ESAD procedure itself. A recent article by H. Olender et al.[31] has reported an increase in active surface area of aged fuel cell electrodes as the result of potentiostatic cycling.

Although performed under far different conditions (85% phosphoric acid at 105°C) than our own ESAD procedure (4M sulfuric acid at 25°C), the Olender work[31] still casts doubt upon measurements of active surface area made through this technique.

A third technique, which is suitable for the direct measurement of average platinum crystallite size, is X-ray diffraction line broadening. This method, which provides a means of determining the degree to which platinum sintering has occurred, is a destructive technique that can be used only at the completion of a test program. Furthermore, it determines the average particle size of all the platinum present, including crystallites that for reasons of position or poor electrical contact do not contribute to cell performance.

Although none of the above techniques, taken individually, can unequivocally determine the rate of platinum sintering, they are complementary. Taken together, they provide good evidence of success or failure. The first two of these techniques have been used to evaluate the five catalyzed supports selected for 1000-hour tests, and the third has also been applied to the two supports subjected to 3000-hour tests.

Results of 1000-Hour Tests

The loss of active surface area as a function of time, determined by the ESAD procedure, is graphically illustrated in Figure 14 for all five test materials. Figure 15 illustrates the performance changes with time of the five test materials by plotting current density at constant cathode potential, +650 mV versus RHE. It should be noted that although both performance and active surface area decrease as a function of time for all five materials, the comparative performances of the individual test materials do not correlate well with their respective surface-area values. For example, the test electrode fabricated from VFeN-15 exhibits the lowest specific surface area for platinum of any of the five electrodes. The performance of this cathode at the 400-hour mark, however, is superior to all but the electrode fabricated from GFeO-15-CO.

A problem was encountered during the ESAD test procedure performed on VFeN-15 at the 400-hour mark. During the course of the ESAD, the reference electrode failed, subjecting the test electrodes to high potentials. This, in turn, caused gas bubbles to form within the catalyst layer, which lifted it off its carbon paper base. Such damage is manifested by the discoloration of the otherwise colorless acid electrolyte. The fuel cell containing the VFeN-15 support was disassembled and rebuilt with new electrodes fabricated from the same batch of VFeN-15 support material. This new fuel cell was operated continuously; however, no electrochemical surface-area determination procedure was performed on this electrode during its lifetime.

The performance of this second fuel cell using support VFeN-15 is also reported in Figure 15. An initial break-in period is exhibited by this material that extends well beyond the 400-hour duration of the first test. It is apparent from the performance curves for the two VFeN-15 cathodes (a and b) that the ESAD procedure does have an effect on the initial break-in period. VFeN-15 (a) was subjected to an ESAD procedure at 24 and 80 hours, the latter corresponding to the point of maximum observed performance. VFeN-15 (b), however, was not subjected to the ESAD procedure at all, and its maximum performance is reached at about 200 hours into the test. It should be noted that the performance of VFeN-15 (b) levels off after about 700 hours to a value close to that exhibited by VFeN-15 (a) at 400 hours. This suggests that although the ESAD procedure may accelerate the break-in process, it does not significantly alter the long-term performance of the electrode.

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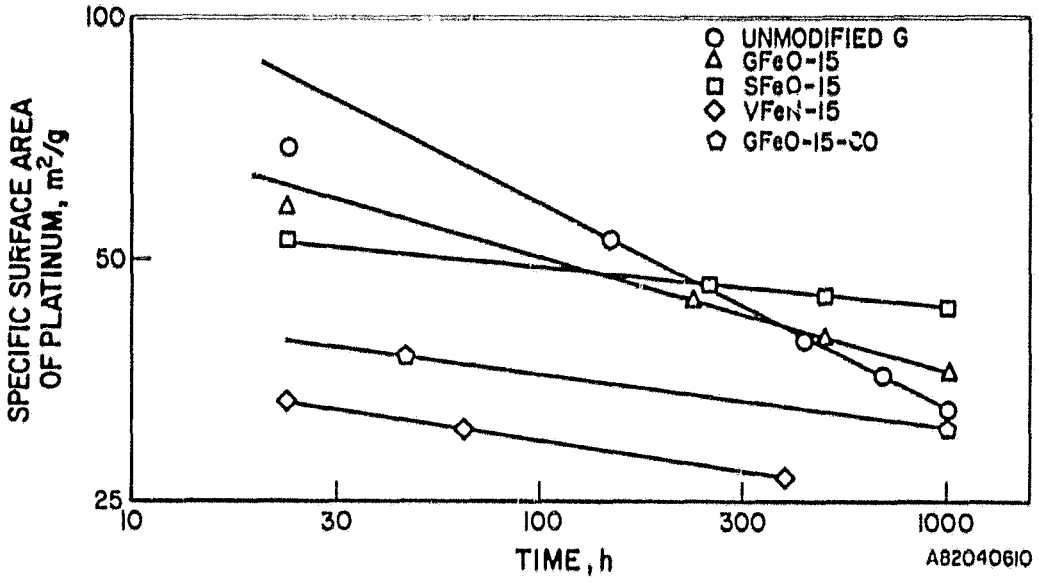

Figure 14. PLATINUM SURFACE-AREA LOSS WITH TIME AS MEASURED BY ESAD PROCEDURE

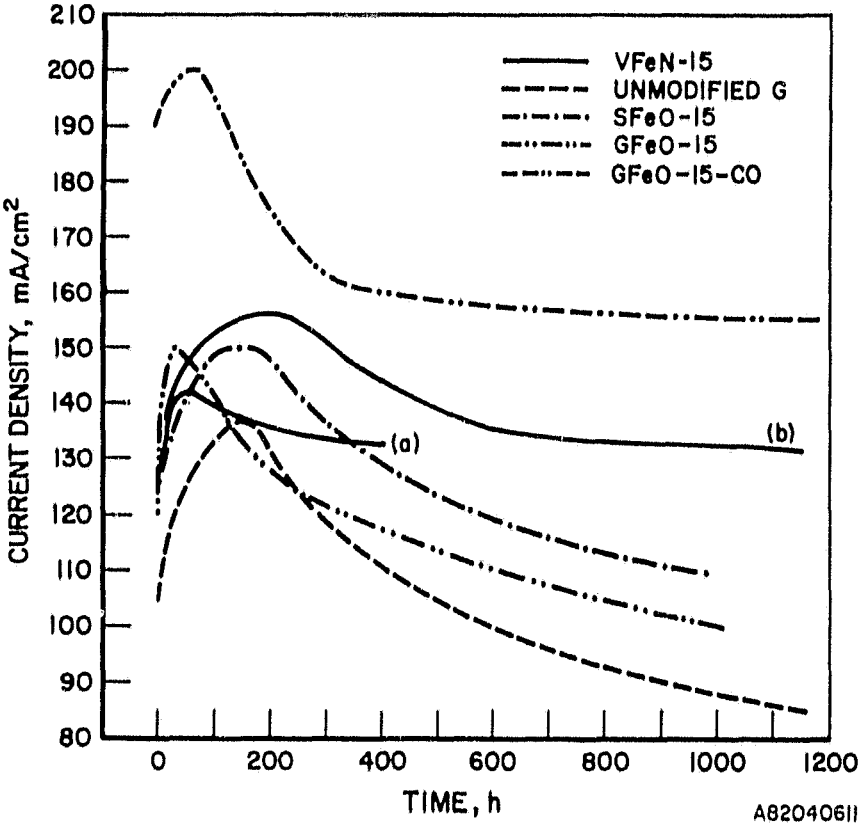

Figure 15. DECREASE IN CATHODE PERFORMANCE AS A FUNCTION OF TIME AT A CONSTANT CATHODE VOLTAGE OF 650 mV VS. RHE

Task 5. 3000-Hour Tests on VFeN-15 and GFeO-15-CO

It can be seen from Figure 15 that the performance of phosphoric acid fuel cell cathodes fabricated from VFeN-15 and from GFeO-15-CO were superior to the other three test electrodes through 1000 hours of testing. As a consequence, evaluation of these two cathodes was continued, the goal being 3000 hours of dynamic testing. Figure 16 illustrates the long-term performance of these two test electrodes as a function of time. The performance of VFeN-15 is fairly stable through 2380 hours but deteriorates slowly thereafter. The dynamic testing of this electrode was terminated at 2670 hours, when the fuel cell began leaking acid. The performance of the fuel cell containing cathode catalyst/support material GFeO-15-CO, on the other hand, remained stable through 3035 hours. The erratic performance following the 1017-hour mark was most likely caused by the ESAD procedure performed at that time.

After completion of the long-term tests, these fuel cells were disassembled and the cathodes recovered. That portion of the catalyst layer which was exposed to the phosphoric acid was cut from the electrode and subjected to an X-ray diffraction line broadening study to determine the average size of the platinum crystallites. Similarly sized samples of Teflon-bonded catalyzed supports were trimmed from unused electrodes and used as controls. The results are listed in Table 6.

Table 6. RESULTS FROM X-RAY DIFFRACTION LINE BROADENING STUDIES OF VFeN-15 AND GFeO-15-CO

Catalyzed Support	Testing Duration, h	Average Crystallite Diameter, Å
VFeN-15	0	40
VFeN-15 (a)	402	92
VFeN-15 (b)	2670	152
GFeO-15-CO	0	56
GFeO-15-CO	3035	65

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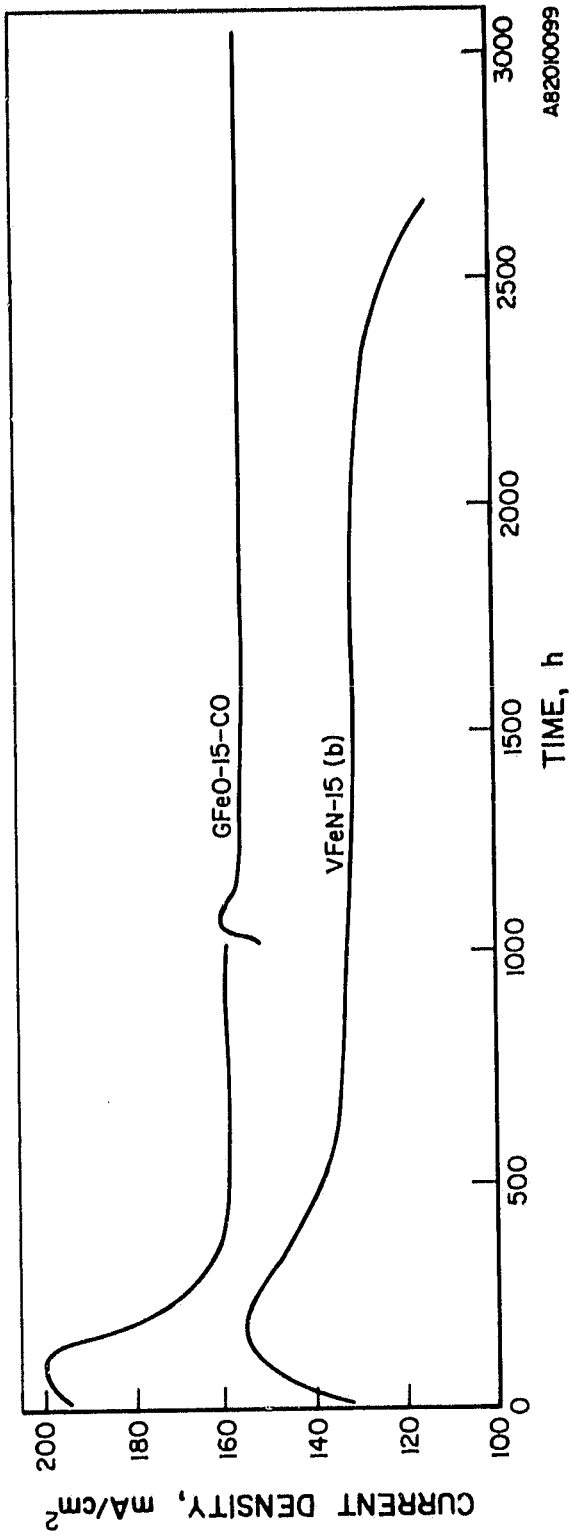

Figure 16. PERFORMANCE OF CATHODES CATALYZED WITH VFeN-15 AND GFeO-15-CO AS A FUNCTION OF TIME

CONCLUSIONS

In general, the results of the 24-hour static tests and the 1000-hour dynamic tests show that the method for catalytic oxidation of graphitic carbons used here does reduce the rate of platinum surface-area loss experienced on phosphoric acid fuel cell cathodes operated at 650 mV positive of RHE in 100% acid at 191°C. But the reduction in the rates of active surface-area loss and the rate of decrease in cell performance with time cannot be attributed unequivocally to the formation of etch pits. For example, the relative performances at 1000 hours of cathodes fabricated from supports VFeN-15, SFeO-15, GFeO-15, and unmodified G correlate as well with the BET surface area of these modified supports as it does with the pore structure. Thus, the reduction of active surface area with time may be as much the result of increased surface area of the support and increased tortuousness of the path of migrating crystallites as it is the trapping of crystallites in etch pits. More importantly, the reduction in active surface-area loss with time that can be achieved by this process alone is not large enough to be considered a solution to the problem of sintering. Nevertheless, when this method of catalytic oxidation is combined with the method of Jalan[30] for depositing carbon around platinum crystallites, an extremely stable catalyzed support is produced, which shows good long-term performance and little propensity for platinum sintering.

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